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ning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR MAKING MVTR RESIN

(57) Abstract: The present invention is directed to producing a resin which, when formed into a film, has excellent gas barrier and/or moisture barrier (low MVTR) properties. Further, the resin has a relatively high molecular weight distribution, preferably above 6, and has excellent processability/extrudability. The resin is produced using a cyclopentadienyl chromium compound, preferably a mono CpCr compound, on a support, preferably a silica support. A particularly preferred catalyst for use in the present invention comprises pentamethylcyclopentadienyldimethylchromiumpyridine. Preferably, the catalyst is used in a slurry polymerization process.



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1 **PROCESS FOR MAKING MVTR RESIN**

2 FIELD OF THE INVENTION

3 The present invention relates to a process for producing ethylene polymers
4 having excellent resistance to moisture vapor transmission when the resin is
5 formed into a film. Further, the process of the present invention produces
6 MVTR resins which have ease of processing into a film packaging product.

7 The process of the present invention preferably uses a catalyst comprising a
8 cyclopentadienyl chromium compound supported on a solid refractory
9 material, in slurry or gas phase reaction conditions.

10 BACKGROUND OF THE INVENTION

11 Polymeric composition for uses such as food packaging and other
12 applications where good barrier properties against moisture ingress have
13 been known for many years. Use of HDPE (high density polyethylene) for this
14 purpose is disclosed in Kirk-Othmer, 3rd Edition, page 489. However, many
15 HDPE polymers are not readily processable, such as by extrusion, to form
16 packaging products.

17 It is desirable to have an HDPE that has excellent moisture vapor
18 transmission resistance (MVTR) and also is relatively easy to process into a
19 packaging product, such as a film.

20 The general theory of permeation of a gas or liquid through a polymer film is
21 that the permeation rate is the product of a diffusion term and a solubility
22 constant of the gas-liquid in the polymer, each of which is often independent
23 of the other. The process of permeation through a polymeric barrier involves
24 four steps: absorption of the permeating species into the polymer wall;

1 solubility in the polymer wall; diffusion through the wall along a concentration
2 gradient; and desorption from the outer wall.

3 There are certain molecular structures that lead to good barrier properties in
4 polymers. A practical problem, however, is that the property that might result
5 in a good gas barrier very often also results in a poor water barrier. Polarity is
6 a case in point. Highly polar polymers such as those containing many
7 hydroxyl groups [poly(vinyl alcohol) or cellophane] are excellent gas barriers
8 but also are among the poorest water barriers. In addition, they become poor
9 gas barriers when plasticized by water. Conversely, very non-polar
10 hydrocarbon polymers such as polyethylene have excellent water barrier
11 properties and poor gas barrier properties. It is generally thought that in order
12 to be a truly good barrier polymer, the material must have: some degree of
13 polarity such as contributed by a nitrile, ester, chlorine, fluorine, or acrylic
14 functional groups; high chain stiffness; inertness; close chain-to-chain packing
15 by symmetry, order, crystallinity, or orientation; some bonding or attraction
16 between chains; high glass transition temperature (T_g).

17 In some prior instances, co-extruded film including a polyolefin layer and polar
18 resin layer such as EVOH have been modified to improve water barrier
19 properties by including other substances, such as a wax. Thus, according to
20 U.S. Patent 5,141,801, the barrier properties of a co-extruded film having a
21 crystalline polyolefin surface layer can be improved substantially by
22 incorporating a wax into the polyolefin. The film has an interior polymer layer
23 that prevents migration of the wax to the other surface of the film so that wax
24 does not interfere with the printability or heat sealability of the other surface.
25 The wax-containing polyolefin layer also protects the interior layer from
26 adverse effects of moisture, such as when the interior layer comprises EVOH.
27 An interior layer of EVOH may be sandwiched between wax-containing
28 polyolefin layers to fully protect it from moisture.

1 Major processes for producing PE resins, including HDPE, include solution
2 polymerization, slurry polymerization and gas phase polymerization.
3 Catalysts for these processes include Ziegler-Natta catalysts, Cr catalyst
4 (either in homogeneous form or on a solid support), and, more recently,
5 homogeneous or supported metallocene catalysts. The metallocene catalysts
6 can be either mono or bis cyclopentadienyl (Cp) ligands on a transition metal,
7 such as Ti, Zr, Hf, Cr, etc. The Cp ligands in turn can be substituted by
8 various groups.

9 CpCr catalysts are disclosed in U.S. Patents 5,240,895; 5,302,674;
10 5,320,996; 5,393,720; 5,399,634; 5,418,200; and 5,593,931.

11 U.S. Patent 5,418,200, for example, discloses ethylene polymerization using
12 various CpCr +3 valence compounds on a refractory support, such as silica.
13 The '200 patent states that the polymers produced have a polydispersity or
14 molecular weight distribution (MWD) greater than 10, and that the polymers
15 have improved ease of processing, better melt behavior, and other desirable
16 properties such as impact resistance and environmental stress crack
17 resistance. Also, the '200 patent points out that large blow molded products
18 are superior when made with high MWD polymers, and that film is more
19 puncture resistant when made from polymer with a high MWD.

20 The '200 patent does not disclose MVTR properties for film made from the
21 polymers produced per the '200 process.

22 WO 96/19527 (PCT/US95/16570) discloses polyethylene films of
23 advantageous (low) MVTR, wherein the polyethylene resin used to make the
24 film is produced using a metallocene catalyst. The metallocene catalysts are
25 not specifically described in WO 96/19527, but reference is made to
26 co-pending application U.S. Serial No. 08/093,501 for disclosure of the
27 metallocene catalysts useful in the '527 patent application.

1 According to the '527 patent application, the polyethylene resin has a density
2 in the range of from about 0.935 to about 0.965 g/cm³, a M_w/M_n less than
3 about 3, and an article made using the resin has a water vapor transmission
4 rate less than 0.54 g•mil/100 in²/day (0.183 g/mm/m²/day), preferably less
5 than 0.4 g•mil/100 m² day (0.135 g/mm/m²/day).

6 Thus, the films made from the polyethylene according to the '527 patent
7 application have a MWD or polydispersity below 3.

8 U.S. Patent 5,183,792 is directed to producing polyolefin resin using a catalyst
9 comprising chromium and titanium supported on silica. The polymer
10 produced has a high melt index and a narrow molecular weight distribution
11 (MWD). The narrow MWD is indicated in U.S. Patent 5,183,792 as helpful in
12 achieving a low MVTR. As stated in the '792 patent at column 4, lines 35-40:
13 "The product will have a high melt index (MI) and a low high load melt
14 index/melt index ratio (HLMI/MI) and, as is observed when these two
15 properties are high and low respectively, a low water vapor transmission."

16 Also, in *Plastics Technology*, August 1999, in an article by J. Krohn et al. titled
17 "Keep It Dry, Optimize Moisture Barrier in PE Films", at pages 60-61, the
18 authors state "Thus, structure 3 excelled in barrier because it was the only
19 one to have a skin layer of higher MI resin with narrower MWD, both of which
20 contribute inherently to better barrier."

21 SUMMARY OF THE INVENTION

22 According to the present invention, a process is provided for making an
23 ethylene homopolymer having a polydispersity above 4, and wherein the
24 homopolymer is suitable for producing a film having a high barrier to
25 transmission of water or gas, or both, which process comprises contacting
26 ethylene with a catalyst comprising a cyclopentadienyl chromium hydrocarbyl

1 compound on a solid support, under slurry or gas phase polymerization
2 conditions.

3 The process of the present invention is especially advantageous in producing
4 resins which have an MVTR less than 0.4, preferably less than 0.3, still more
5 preferably below 0.25 grams of water per 100 square inches of film per day,
6 for a 1 mil (one thousandth of an inch) thick film.

7 Preferably, the resins produced in accordance with the present invention have
8 a polydispersity or MWD above 4, more preferably between 4.5 and 12, and
9 most preferably between 4.7 and 7.5.

10 Preferred catalysts for use in the process of the present invention are mono or
11 bis cyclopentadienyl chromium compounds, more preferably a mono
12 cyclopentadienyl, on a solid support. Preferably, mono cyclopentadienyl
13 contains one or more substituents. Preferred substituents are hydrocarbyl
14 groups; particularly preferred is cyclopentadienyl substituted with five methyl
15 groups. Preferably the solid support is silica. An especially preferred catalyst
16 for use in the process of the present invention is pentamethyl CpCr(CH₃)₂Pyr
17 on a solid support, where Cp represents cyclopentadienyl, and Pyr represents
18 pyridine. Preferred co-catalysts are alumoxanes, especially isobutyl
19 alumoxane (IBAO). Preferred catalysts for use in the present invention are
20 described in more detail below.

21 We have found that use of catalysts such as the aforementioned especially
22 preferred catalyst, under process conditions as described herein, produces
23 substantially linear polyethylene of density at least 0.955 g/cc, with nearly all
24 of the terminal groups of the polyethylene polymer saturated. Preferably, the
25 process conditions are selected to allow the catalyst to react under
26 mechanisms that produce predominately saturated end groups, that is, the
27 methyl end group to olefin end group ratio relatively high, at least 10, and

1 preferably greater than 15, as measured by FTIR (Fortier Transform Infrared
2 spectroscopy).

3 Preferred process conditions, particularly when using the aforementioned
4 especially preferred catalyst, include polymerization reaction zone
5 temperature between 50°C to 100°C, more preferably 70°C to 90°C, with a
6 slurry ethylene concentration of 8-15 weight percent. Hydrogen is a preferred
7 chain transfer agent.

8 Other particularly preferred process conditions are related to the extrusion
9 and pelletization process, and the film process.

10 Ideal compound conditions, or pelletization process are those that do not alter
11 the chemical structure of the polymer; preferably cross-linking or long chain
12 branching are kept to minimum.

13 Among other factors, the present invention is based on our finding that
14 unexpectedly low MVTRs can be achieved from relatively high MWD resins,
15 greater than 4 MWD, wherein the resin is produced from CpCr catalysts as
16 described in more detail below. The resins produced by the process of the
17 present invention have excellent processability while still achieving excellent
18 MVTR properties.

19 BRIEF DESCRIPTION OF THE DRAWINGS

20 Figure 1 is a schematic diagram showing a film of five layers that may be
21 used in an application requiring low moisture vapor transmission rate (low
22 MVTR).

23 Figure 2 is a schematic diagram showing a three-layer film that may be used
24 in an application requiring low moisture vapor transmission rate (low MVTR).

1 DETAILED DESCRIPTION OF THE INVENTION

2 One important aspect of the present invention is the achievement of a process
3 for producing a polyolefin resin which, when formed into a film, has a low
4 MVTR, while also achieving particularly attractive processing characteristics
5 for the resin.

6 MVTR (Moisture Vapor Transmission Rate) or WVTR (Water Vapor
7 Transmission Rate), as it is sometimes called, is determined for a resin in a
8 two-step process (three-step if one includes the pelleting step for the resin
9 fluff from the reactor), involving extrusion and measurement. Resin produced
10 in a slurry or gas phase process is first compounded into pellets which are
11 extruded into film using a blown or cast film extrusion method. Since
12 extrusion conditions have a significant effect on the MVTR exhibited,
13 extrusion temperatures, extruder output rates, cooling rates, film gauge, and,
14 in the case of blown film, blow-up ratio, are controlled during extrusion of the
15 resin and held constant when comparing the MVTR properties of two or more
16 resins.

17 Following the extrusion of the resin into film, the actual measurement of
18 MVTR is performed using a Mocon Permatran-W3/31 MVTR testing system,
19 or equivalent. The Mocon instrument for measuring water permeability was
20 developed by Modern Controls, Inc. To accomplish the MVTR measurement,
21 a 10 x 10 cm sample is cut from a random area of the film. The sample is
22 then mounted in a sample test cell and placed in the Mocon Permatran W3/31
23 unit. In the unit, the test film is exposed to a constant continuous flow of dry
24 nitrogen gas across one side of the film, exhaust side, and a constant
25 continuous flow of controlled humidity nitrogen gas across the other side,
26 carrier side. Water vapor passes from the humidified nitrogen side of the test
27 cell through the film and into the dry nitrogen side of the test cell. A
28 modulated infrared photodetection system on the exhaust side of the test cell
29 measures the variation in the absorption of infrared energy caused by the

1 water vapor which has transmitted through the film. By comparing the
2 amplitude of the output signal obtained from the infrared photodetection
3 system mounted on the test cell with the amplitude of a signal from a
4 reference cell in the same instrument containing a film with a known
5 transmission rate, the transmission rate of the test film is determined.

6 By convention, the value obtained for MVTR is expressed as grams of water
7 transmitted per 100 square inches per one mil (one thousandth of an inch)
8 thickness in a 24-hour period (or, in metric system, grams of water transmitted
9 per square meter per mm thickness in a 24-hour period).

10 The resins produced by the process of the present invention have a relatively
11 high MWD. MWD is the ratio of the weight average molecular weight (M_w) to
12 the number average molecular weight.

13 Preferred means of determining M_n and M_w is by Gel Permeation
14 Chromatography (GPC) which is also commonly known as Size Exclusion
15 Chromatography (SEC). For the purpose of references to M_n and M_w in this
16 application, molecular weight is determined using a Waters 150°C liquid
17 chromatograph, three linear mixed bed chromatographic columns, and hot
18 carrier solvent of 1, 2, 4 trichlorobenzene (TCB) at 150°C temperature. The
19 GPC elution volume is converted to the linear-equivalent polyethylene
20 molecular weight (M) by way of a standard calibration method using a
21 high-density linear polyethylene standard of known M_w , M_n values and a broad
22 molecular weight distribution. Equation (1) below is used to calculate the
23 polymer weight fraction (W) of different molecular weights existed in the GPC
24 effluent as detected by an online differential refractometer signal (RI).
25 Equations (2) and (3) are used to calculate the M_w and M_n values of any
26 unknown sample using the predetermined M values from the GPC calibration
27 curve.

28

$$(W)_i = \frac{(RI)_i}{\sum (RI)_i} \quad (1)$$

$$M_w = \left[\frac{\sum M_i * (W)_i}{\sum (W)_i} \right] \quad (2)$$

$$M_n = \left[\frac{\sum (W)_i}{\sum (W/M)_i} \right] \quad (3)$$

Another important aspect of the present invention is the catalyst which is used for forming the MVTR resin. As indicated above, the preferred catalyst used in the present invention is a cyclopentadienyl chromium compound on a support.

As used herein, the term "cyclopentadienyl" refers to unsubstituted cyclopentadienyl. However, the cyclopentadienyl ring may contain one or more substituents, preferably substituents which do not interfere with the Cr (chromium) compound's ability to function as an alpha-olefin polymerization catalytic site. Examples of substituted cyclopentadienyl include pentamethylcyclopentadienyl, methylcyclopentadienyl, t-butylcyclopentadienyl, and pentaphenylcyclopentadienyl, as well as compounds where the substituent forms a multi-cyclic ring with the cyclopentadienyl ring. Examples of these multi-cyclic rings include indenyl and fluorenyl rings. For the sake of simplicity, the abbreviation "Cp" will be used herein to refer to unsubstituted cyclopentadienyl. However, substituted Cp groups, including indenyl, which in turn may be substituted, are preferred for use in the present invention. Pentamethylcyclopentadienyl is an especially preferred substituted Cp. Indenyl is treated as a substituted Cp for purposes of the present patent application.

Preferably, the Cr metal atom in the CpCr compound has an oxidation state of +3 in the catalyst as produced.

1 Preferably, these CpCr compounds have, in addition to one cyclopentadienyl
 2 group, at least one hydrocarbyl group bonded to the metal atom. As used
 3 herein, the term "hydrocarbyl" refers to alkyl, alkenyl, aryl, aralkyl and alkaryl
 4 radicals and the like. Exemplary hydrocarbyl radicals include, but are not
 5 limited to, methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, neopentyl,
 6 isobutyl, heptyl, octyl, nonyl, decyl, cetyl, phenyl, benzyl, and other similar
 7 groups. Additionally, organosilyl groups, such as trimethylsilyl methyl, i.e.,
 8 $(\text{CH}_3)_3\text{SiCH}_2-$, and the like can be used. If more than one hydrocarbyl group
 9 is bonded to the metal atom, they can be independent or linked, i.e., they can
 10 form a 3-, 4-, 5-, 6-, 7-membered metallocycle. Preferably, the hydrocarbyl
 11 group is sigma bonded to the Cr metal. Other functional substituents which
 12 may be used on the Cp include ER, where E=O, or S; ER₂, where E=B, N, or
 13 P; and SiR₃. R is an organic moiety.

14 In addition to the cyclopentadienyl and hydrocarbyl groups, the Cr compounds
 15 used in the present invention may also contain one or more sigma donor
 16 stabilizing ligands. These ligands contain an atom, such as oxygen, nitrogen,
 17 phosphorus or sulfur, which has a non-bonded electron pair. Examples of
 18 these ligands include, but are not limited to, ethers, amines, phosphines and
 19 thioethers. Ethers such as tetrahydrofuran (THF) and amines such as
 20 pyridine are preferred. Compounds with pyridine are most preferred for use in
 21 the process of the present invention.

22 Examples of the Cr compounds useful in this invention include, but are not
 23 limited to, compounds having the following general formulas:



1 wherein $(C_5(R')_5)$ is a cyclopentadienyl or substituted cyclopentadienyl ring;
2 R' is at each independent occurrence hydrogen, a hydrocarbyl radical having
3 1-20 carbon atoms, or adjacent R' groups may together form one or more
4 rings;

5 X is a hydrocarbyl radical having 1-20 carbon atoms (for example, a
6 monovalent saturated aliphatic or alicyclic radical or a monovalent aromatic
7 radical, or combinations thereof; X , in addition, may be a monovalent
8 hydrocarbyloxy, amido, phosphido or sulfido radical or combinations thereof:

9 $a = 1$ or 2 , $b = 1$ or 2 where $a + b = 3$;

10 $c = 1$ or 2 with the proviso that when $c = 2$ then X is alkyl;

11 L is at each independent occurrence a sigma donor stabilizing ligand;

12 $m = 1$ to 2 inclusive; and

13 A is an anion.

14 Examples of compounds having Formula (I) above include, but are not limited
15 to, pentamethyl $CpCr(CH_3)_2(THF)$, pentamethyl $CpCr(Bzyl)_2(THF)$,
16 pentamethyl $CpCr(Bzyl)_2(Pyr)$, pentamethyl $CpCr(CH_3)_2(Pyr)$, pentamethyl
17 $CpCr(TMSM)_2(Pyr)$, pentamethyl $CpCr(TMSM)_2$, pentamethyl
18 $CpCr(CH_3)_2(DMAP)$, pentamethyl $CpCr(CH_3)_2(PMe_2Ph)$, pentamethyl
19 $CpCr(CH_3)_2(3,5-Lutidine)$, and pentamethyl $CpCr(CH_3)_2(DMAP)$, where Bzyl
20 is benzyl, Pyr is pyridine, TMSM is trimethylsilylmethyl, DMAP is
21 N,N-dimethylaminopyridine, and PMe_2Ph is dimethylphenylphosphine.

22 Further examples of the Cr compounds preferred for use in the process of this
23 invention include monomeric Cr compounds, dimeric Cr compounds, and
24 cationic Cr compounds. A preferred monomeric Cr compound is pentamethyl

1 CpCr(Bzyl)₂(THF), [pentamethyl CpCr(CH₃)₂]₂ is a preferred dimeric
2 compound, and a preferred cationic compound is [pentamethyl
3 CpCrCH₃(THF)₂]⁺[BPh₄]⁻. Especially preferred compounds are pentamethyl
4 CpCr(CH₃)₂(Pyr), pentamethyl CpCr(CH₃)₂(3,5-Lutidine) and pentamethyl
5 CpCr(CH₃)₂(PMe₂Ph).

6 Several articles, namely, Theopold, *J. Am. Chem. Soc.* (1988) 110, 5902
7 "Cationic Chromium (III) Alkyls as Olefin Polymerization Catalysts", Theopold,
8 *Acc. Chem. Res.* (1990), 23, 263 "Organochromium (III) Chemistry: A
9 Neglected Oxidation State", and Thomas et al., *J. Amer. Chem. Soc.*, 113
10 (1991), p. 893 et seq. (all of which are incorporated herein by reference)
11 describe syntheses useful in making some of the Cr compounds useful in the
12 process of this invention. Similar procedures can be used to make related
13 compounds.

14 In preferred catalyst systems used in the process of the present invention, an
15 organo chromium compound is deposited on an inorganic support. Suitable
16 inorganic metal oxide supports include silica, alumina, silica-alumina mixtures,
17 thoria, zirconia, magnesium oxide and similar oxides. Suitable inorganic
18 metal phosphates include aluminum phosphate, zirconium phosphate,
19 magnesium-containing alumina phosphate and alumina aluminum phosphate.
20 Silicas, aluminum phosphates and alumina aluminum phosphates are
21 preferred. Suitable silica supports include Davison 952, Davison 948,
22 MS 3030 and MS 3050, Crosfield EP-10 and Crosfield EP17MS. Further
23 examples of useful supports are the following: alumina aluminum phosphates
24 with aluminum to phosphorus ratios of about 5:1 to 1:1 as disclosed in U.S.
25 Patents 4,080,311 and 4,219,444; magnesia-alumina-aluminum phosphates
26 as described in U.S. Patent 4,210,560; zinc oxide-cadmium oxide-alumina-
27 aluminum phosphates such as those disclosed in U.S. Patent 4,367,067; and
28 the calcium, barium, and/or strontium oxide-alumina-aluminum phosphates
29 described in U.S. Patents 4,382,877 and 4,382,878. The acidity of these
30 supports can be adjusted by judicious inclusion of basic metals such as alkali

1 and alkaline earth metals (Ca, Be, Mg, K, Li) to counteract excessive acidity.
2 Other useful supports include magnesium halides, particularly magnesium
3 chloride, such as those described in "Transition Metals and Organometallics
4 as Catalysts for Olefin Polymerization" (1988, Springer-Verlag) edited by W.
5 Kaminsky and H. Sinn and "Transition Metal Catalyzed Polymerizations-
6 Ziegler-Natta and Metathesis Polymerizations" (1988, Cambridge University
7 Press) edited by R. Quirk.

8 The supports useful in this invention should have a high surface area. In
9 general, these supports should have characteristics listed in the following
10 table:

Property	Broad Range	Preferred Range	More Preferred Range
Surface area, m ² /g	25-600	100-400	250-350
Pore volume, cm ³ /g	0.25-4	0.7-3	1.5-2.0
Mean particle diameter, microns	20-200	25-140	30-70

11

12 Preferably, the pore size distribution is narrow, with a significant percentage of
13 the pores in the range 150-200 Angstroms. It is also desirable that the
14 support be substantially anhydrous before the Cr compound is deposited on it.
15 Thus, it is desirable to calcine the support prior to deposition of the Cr
16 compound.

17 The supported catalysts used in this invention are readily prepared by
18 techniques known in the art. For example, a solution of the Cr compound in
19 aliphatic, aromatic or cycloaliphatic hydrocarbons, or ethers such as diethyl
20 ether or tetrahydrofuran can be stirred with the support until the Cr compound
21 is adsorbed on or reacted with the support. The amount of Cr compound
22 relative to the amount of support will vary considerably depending upon such

1 factors as the particle size of the support, its pore size and surface area, the
2 solubility of the Cr compound in the solvent employed, and the amount of Cr
3 compound which is to be deposited on the support. However, in general, the
4 amount of Cr compound used is adjusted so that the final metal content
5 (calculated as the element), relative to the support, is in the range of from
6 about 0.01 to about 5 weight percent. In most cases, the most desirable level
7 is in the range of about 0.1 to about 1.5 weight percent.

8 The activity of many of the supported Cr compounds used in the process of
9 this invention is significantly increased when they are employed in conjunction
10 with a co-catalyst. The co-catalysts useful in the practice of the present
11 invention are Group 2 and Group 3 metal alkyls. As used herein, the term
12 "Group 2 and Group 3 metal alkyls" refers to compounds containing a metal
13 from Group 2 or Group 3 of the Periodic Table (such as Mg, Zn, B or Al) to
14 which is bonded at least one alkyl group, preferably a C₁ to C₈ alkyl group.
15 Suitable Group 2 and Group 3 metal alkyls include dialkyl magnesium, dialkyl
16 zinc, trialkylboranes, and aluminum alkyls. Suitable aluminum alkyls include
17 trialkylaluminums (such as trimethylaluminum, triethylaluminum,
18 triisobutylaluminum and trioctylaluminum). Trialkylaluminum with alkyl groups
19 of four carbons or greater are preferred. Other aluminum alkyls useful in the
20 practice of the present invention include alkylaluminum alkoxides (such as
21 diethylaluminum ethoxide and ethylaluminum diethoxide), and alkylaluminum
22 halides (such as diethylaluminum chloride, diethylaluminum bromide,
23 diethylaluminum iodide, diethylaluminum fluoride, ethyl aluminum dichloride,
24 ethyl aluminum dibromide, ethyl aluminum diiodide, ethyl aluminum difluoride,
25 and ethyl aluminum sesquichloride).

26 Preferred aluminum alkyls are aluminoxanes, including those represented by
27 the general formula (R-Al-O)_n for the cyclic form and R(R-Al-O)_nAlR₂ for the
28 linear form. In these formulas, R is, at each independent occurrence, an alkyl
29 group (such as methyl, butyl, isobutyl and the like) preferably with more than
30 two carbon atoms, more preferably with 4-5 carbon atoms, and n is an

1 integer, preferably from 1 to about 60. Most preferably, R is an isobutyl
2 group. Mixtures of linear and cyclic aluminoxanes may also be used.
3 Examples of aluminoxanes useful in this invention include, but are not limited
4 to, ethyl aluminoxane, isobutyl aluminoxane, and methyl aluminoxane, and
5 mixtures thereof. Aluminoxanes (also known as "alumoxanes") suitable for
6 use in this invention are described in Pasynkiewicz, "Alumoxanes: Synthesis,
7 Structure, Complexes and Reactions," Polyhedron 9, p. 429 (1990), which is
8 incorporated by reference herein in its entirety.

9 The preferred Group 2 and Group 3 metal alkyls are aluminoxanes and the
10 trialkylaluminums.

11 When used, the Group 2 and Group 3 metal alkyls are used in a Group 2 or
12 Group 3 metal alkyl to Cr compound mole ratio of from about 1:1 to about
13 1000:1. The preferred mole ratio is from about 1:1 to about 100:1.

14 The process of the present invention may be carried out in either solution,
15 slurry or gas phase polymerization processes, and preferably is carried out in
16 a slurry or gas phase process. After the catalyst has been formed, the
17 polymerization reaction is conducted by contacting the monomer charge with
18 a catalytic amount of the catalyst at a temperature and at a pressure and
19 ethylene concentration sufficient to initiate the polymerization reaction. As
20 indicated above, preferably substantially linear polyethylene is produced in the
21 present invention. For a slurry process, an organic solvent may be used as a
22 diluent and to facilitate heat transfer. The polymerization reaction is carried
23 out at temperatures of from about 30°C or less up to about 250°C or more,
24 depending on the equipment design and on the operating pressure, and the
25 particular catalyst being used. Preferably, the temperature is from about 60°C
26 to about 125°C, more preferably 60°C to 100°C. The pressure is dependent
27 on ethylene concentration and is sufficient to initiate the polymerization of the
28 monomer charge, and can be from atmospheric up to about 1000 psig, more
29 preferably about 20 to about 800 psig. For a slurry or solution polymerization,

1 the ethylene concentration in the range of 4-20 weight percent of the solvent
2 or diluent phase is preferred.

3 When the catalyst is used in a slurry or solution type process, an inert solvent
4 or diluent medium is used. The solvent or diluent should be one which is inert
5 to all other components and products of the reaction system, and be stable at
6 the reaction conditions being used. It is not necessary, however, that the inert
7 organic solvent medium also serve as a solvent for the polymer produced.
8 The inert organic solvents which may be used include saturated aliphatic
9 hydrocarbons (such as hexane, heptane, pentane, isopentane, isooctane,
10 purified kerosene and the like), saturated cycloaliphatic hydrocarbons (such
11 as cyclohexane, cyclopentane, dimethylcyclopentane, methylcyclopentane
12 and the like), aromatic hydrocarbons (such as benzene, toluene, xylene and
13 the like), and chlorinated hydrocarbons (such as chlorobenzene,
14 tetrachloroethylene, o-dichlorobenzene and the like). Particularly preferred
15 solvents or diluents are isobutane, cyclohexane, hexane and heptane.

16 When the catalyst is used in a gas phase process, preferably it is suspended
17 in a fluidized bed with, e.g., ethylene. Temperature, pressure and ethylene
18 flow rates are adjusted to maintain acceptable fluidization of the catalyst
19 particles and resultant polymer particles. Further descriptions of such a
20 fluidized bed may be found in British Patent 1,253,063, to Karapinka, which is
21 incorporated by reference herein.

22 The resin produced by the process of the present invention is used to produce
23 a film. Referring now to Figures 1 and 2, two alternate preferred product
24 MVTR film constructions are shown. Figure 1 is a five-layer coextruded
25 MVTR film construction. Figure 2 is a three-layer coextruded MVTR film.
26 Known means may be used for coextruding resin to form the respective layers
27 of the coextruded MVTR film illustrated in Figures 1 and 2. Also, the resin
28 produced in accordance with the process of the present invention may be
29 used in a monolayer.

1 One advantage we have found for the resins produced in accordance with the
2 present invention is that they may be advantageously used to form film of low
3 MVTR. Further, the resins produced in accordance with the present invention
4 are advantageous in that the same resin may be used for the skin layer of the
5 coextruded construction and the core layer(s). In typical prior art, a higher
6 (2 g/10 min or higher) melt index HDPE resin is used in the skin layer of the
7 construction and a lower (less than 1.5 g/10 min) melt index HDPE resin is
8 used in the core layer(s) in order to achieve lower MVTR than a film using the
9 lower MI in both the skin and core layers.

10 Referring now to Figures 1 and 2, two alternate preferred product MVTR film
11 constructions are shown. Figure 1 is a five-layer coextruded MVTR film
12 construction. Figure 2 is a three-layer coextruded MVTR film. Known means
13 may be used for coextruding resin to form the respective layers of the
14 coextruded MVTR film illustrated in Figures 1 and 2. Also, the resin produced
15 in accordance with the process of the present invention may be used in a
16 monolayer film. However, commercial viability of monolayer applications is
17 generally dependent on heat sealing qualities of HDPE. Applications of the
18 resin produced by the present invention can be made to produce a monolayer
19 film for barrier properties which when laminated to other films or paper to
20 make a finished product, such as a packaging product.

21

22 One advantage we have found for the resins produced in accordance with the
23 present invention is that they may be advantageously used to form film of low
24 MVTR. Further, the resins produced in accordance with the present invention
25 are advantageous in that the same resin may be used for the skin layer of the
26 coextruded construction and the core layer(s). In typical prior art, a higher
27 (2 g/10 min or higher) melt index HDPE resin is used in the skin layer of the
28 construction and a lower (less than 1.5 g/10 min) melt index HDPE resin is
29 used in the core layer(s) in order to achieve lower MVTR than a film using the
30 lower MI in both the skin and core layers.

31

1 Figure 1 illustrates a preferred five-layer construction. The outer layer or
2 outside skin of the film is layer 1. The core layers are layers 2, 3 and 4. The
3 inside layer, which is referred to as the seal layer, and may come into contact
4 with foodstuffs, is layer 5. Preferably, layer 1 is 10% to 20% of the total
5 thickness, layers 2, 3 and 4 preferably are 60% to 80% of the thickness, and
6 layer 5 is 10% to 20% of the thickness of the product film.

7
8 As referenced in the August 1999 issue of *Plastics Technology* in the article
9 "Keep It Dry" and from common knowledge in the MVTR film market, in the
10 five-layer construction, Layer 1, the skin layer or outside layer of the film is
11 generally a HDPE having a melt index of between 2 and 6 g/10 min. The
12 three core layers, Layers 2, 3 and 4 in the figure, generally consist of a HDPE
13 having a melt index between about 0.5 and 1.5, preferably approximately
14 1.0 g/10 min. The core layers can be fed by three separate extruders or may
15 be formed by splitting the stream from one extruder into two or three
16 independent layers prior to or inside the die. As mentioned above, layer 5 in
17 Figure 1 is the seal layer in the coextruded construction. The seal layer may
18 consist of a single resin, such as a high ethylene vinyl acetate copolymer or
19 may be a blend of several resins. Resins used in the seal layer generally
20 demonstrate a low crystallinity and as such do not appreciably contribute to
21 the MVTR performance of the film.

22
23 Figure 2 illustrates an alternate preferred construction, which is three layers.
24 The outer layer or outside skin of the film in Figure 2 is layer a. The core layer
25 is layer b. The inside layer, which is referred to as the seal layer, and may
26 come in contact with foodstuffs, is layer c. Preferably, layer a is 10% to 20%
27 of the total thickness, layer b preferably is 60% to 80% of the thickness, and
28 layer c is 10% to 20% of the thickness of the product film.

29
30 As is the case in the five-layer construction, the three-layer construction
31 generally utilizes a 2 to 6 g/10 min. melt index HDPE, layer a in Figure 2, in
32 the skin layer. The core layer in the three-layer construction, layer b, is a

1 HDPE generally having a melt index of about 0.5 to 1.5, preferably about
2 1.0 g/10 min. The seal layer, layer c, in the three-layer construction generally
3 utilizes the same type of resins and resin blends commonly found in the
4 five-layer construction.

5

6 An unexpected advantage we have found for the resins produced by the
7 present invention is that the same grade HDPE may be used for both layer a
8 and layer b in the three-layer construction and in layers 1, 2, 3 and 4 and
9 achieve substantially equivalent barrier properties to the conventional systems
10 requiring different grades of HDPE in the skin and core layer(s). Using the
11 same grade HDPE is attractive for film manufacturers for convenience in both
12 production of film and the inventory of resin. Since a HDPE resin produced by
13 the present invention eliminates the need for a separate skin and core layer
14 HDPE resin, film processors can reduce the number of HDPE resins they
15 must inventory and the need for tracking two different HDPE resins within the
16 transfer systems of the plant is eliminated.

17

18 We have found that, using the resin produced in accordance with the present
19 invention, the high MI outside skin (layer a in the three-layer coextrusion and
20 layer 1 in the five-layer coextrusion) of 2 MI or greater per the prior art can be
21 replaced by an approximately 1 MI HDPE resin produced in accordance with
22 the present invention. And, the same 1 MI resin can be used for the core
23 layers, and yet still achieve attractive performance, such as low MVTR for the
24 overall film.

25 The following examples are intended to further illustrate the present invention.

EXAMPLESExample 1

A preferred catalyst for use in the process of the present invention is prepared as follows: The pentamethyl $\text{CpCr}(\text{CH}_3)_2(\text{Pyr})$ was prepared following the general description contained in Noh, S.K.; Sendlinger, S.C.; Janiak, C.; Theopold, K. H., *J. Am. Chem. Soc.* (1989), 111, 9127. Lithium cyclopentadienide (0.380 g, 2.67 mmol) was added slowly to a slurry of 1.00 g (2.67 mmol) of $\text{CrCl}_3(\text{THF})_3$ in 50 mL of THF. The resulting blue solution was stirred for 2 hours. Pyridine (0.222 g, 2.80 mmol) was added resulting in the deposition of a light blue solid. Stirring was continued for 1 hour after which was added (dropwise) 2.0 equivalents (3.80 mL of 1.4M solution in Et_2O) of methyllithium. The dark green-brown solution was stirred an additional 0.5 hr. and then taken to dryness under vacuum. The dark solid was extracted into pentane, filtered to remove metal halides, and taken dryness. The remaining solid was re-extracted into pentane, filtered, and the solvent was reduced until microcrystals appeared. The dark brown solution was kept at -40°C overnight resulting in the deposition of black crystals. The crystals were collected and dried under vacuum. Silica (Davison 948) activated at 700°C , 300 g was charged to a flask and 1600 ml heptane was added in an inert atmosphere. The contents are heated to 70°C with mechanical stirring to form a silica slurry.

Then 15 g of the pentamethyl $\text{CpCr}(\text{CH}_3)_2(\text{Pyr})$ was added in 2-3 g aliquots to the silica slurry over the course of 1 hour. The contents of the flask was stirred for 12 hrs. at 70°C . The contents of the flask were cooled to room temperature and filtered with a fritted glass filter. The solid was dried on the filter under vacuum at $40-45^\circ\text{C}$ for 4 hrs. and further dried an additional 10-12 hrs. by passing argon up through the fritted filter at $40-45^\circ\text{C}$. The solid catalyst was then transferred to a receiving vessel.

Example 2Gas Phase

Supported CpCr catalyst, as described in Example 1, was introduced continuously into a 24-inch outside diameter gas phase fluid bed polymerization reactor to polymerize ethylene. Isobutyl aluminoxane (IBAO) was fed to the reactor as a co-catalyst at various Al:Cr ratios including at an atomic ratio of (Al/Cr) of eight. Hydrogen was fed to the reactor to assist in control of the molecular weight of the polyethylene product. The reactor operating conditions were:

Polymerization Temperature	210°F
Polymerization Pressure	300 psig
Ethylene Pressure	260 psi
Gas Phase H ₂ /C ₂ = Molar Ratio	0.025
IBAO Feed Al/Cr Molar Ratio	8
Production Rate PE	22 lbs/hr

The resulting polyethylene product had a density of 0.9640 g/cc, a MI of 0.67 g/10 min, and a melt flow ratio (MFR) of 109.

We have found that resins with low MVTR are produced in accordance with the present invention using gas phase; however, slurry (liquid) phase reaction conditions are preferred as described in the next example.

Example 3Slurry Polymerization

Slurry polymerization of ethylene in isobutane was carried out in a high pressure pilot plant equipped with a 50-gal loop reactor operated in a continuous mode at a pressure of 600 psig and temperature of 180°F to

1 200°F. Operating conditions and product properties are described further
2 below and summarized in Tables A and B below.

3 The catalyst as prepared in Example 1 was continuously injected as an
4 isobutane slurry to the bottom of the loop. The co-catalyst,
5 isobutylalumoxane, IBAO, was continuously metered as a 0.8 wt. % solution
6 in hexane or isopentane at a rate of 100 to 300 cc/hr into the catalyst feed line
7 to provide a 15 to 45 seconds pre-contact and reaction time prior to flowing
8 into the loop reactor.

9 Ethylene and hydrogen were continuously metered into an isobutane feed at
10 the top of the loop. An additional isobutane feed stream was maintained
11 across the face of the circulating pump.

12 The reaction slurry was circulated at a rate of 2300 gal/min via a Sultz
13 Bingham circulating pump. Slurry was discharged from the loop via a letdown
14 valve operated by pressure control, 585 to 600 psi differential.

15 The slurry leaving the loop passed into a flash stage for primary removal of
16 isobutane, ethylene, and hydrogen and into a rotary drier stage for final
17 degassing and transport into collection drums. Gas from the flash stage was
18 continuously analyzed for its makeup. The solid catalyst injection quantity
19 was adjusted to control the desired ethylene content in the reactor at 4 to
20 10 wt. % based on a constant quantity of ethylene and isobutane feed and to
21 maintain a constant production rate of polyethylene. Polyethylene molecular
22 weight was controlled by the hydrogen concentration in the isobutane. The
23 hydrogen feed was adjusted to maintain a constant ratio of hydrogen to
24 ethylene in the reactor, as measured by the gas composition in the flash tank.
25 The polymerization product, the polyethylene fluff, was chemically
26 characterized according to the following methods.

1 The Melt Index was used as a measure of molecule weight and MFR was
2 used as a measure of MWD. MFR was measured according to
3 ASTM 1238-90b as a function of MI and a HLMI. MFR is the ratio of HLMI to
4 MI. HLMI and MI are determined in accordance with the currently approved
5 ASTM method.

6 The density of the fluff and pellets was determined in accordance with
7 ASTM 1928-90. GPC was used for both fluff and pellets to measure
8 molecular weights as M_w , M_n , and MWD. Melting points were determined by
9 DSC according to ASTM E 794.

10 The polyethylene fluff was compounded with an antioxidant, Irganox
11 (registered trademark of Ciba-Geigy) B9355FF, at a level of 400 to 880 ppm
12 weight, into pellets on a Werner Pfleiderer 30 mm twin screw extruder. The
13 typical conditions for pelletization include oxygen exclusion via a nitrogen
14 purge, 55 lbs/hr rate, 200 rpm screw speed; temperature ($^{\circ}\text{F}$) profile over
15 zones 1-6 at 200, 300, 350, 400, 450. The water bath was maintained at near
16 ambient conditions. The pellets were formed into film and the film samples
17 tested according to ASTM F 1249, for MVTR, as reported in Table B.

Table A
Operating Conditions and Resin Properties

Run #	Temp °F	iC ₄ lbs/hr	C ₂ lbs/hr	IBAO cc/hr	C ₂ wt. %	H ₂ /C ₂ mol%/wt. %	Cat Base/Cr, wt. %	MI	MFR	PE, rate lbs/hr
1	190	65	30	600	8.0	0.0020	MS3030/1.0	1.1	53	25
2	185	65	30	300	9.0	0.0019	DAV948/0.8	1.1	45	25
3	205	65	30	300	8.0	0.0019	DAV948/0.8	1.0	57	
4	190	65	30	300	8.4	0.0019	DAV948/0.8	1.0	50	

25
1
2

Table B
Resin, Pellet and Film Data

Run #	Mn	Mw	MWD	P g/cc	Cr/Al ppm/ppm	MVTR	FTIR Methy/Vinyl	MVTR % Control
1	21,500	123,000	5.7	0.963	0.8/13	0.226		17.8
2	23,800	120,000	5.0	0.962	<0.1/12	0.249	21	8.5
3	18,800	132,000	7.0	0.962	1.4/10	0.236		15.2
4	21,900	120,600	5.5	0.963	0.4/12	0.258	17.8	15.5

3

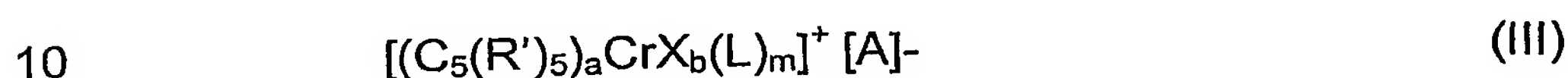
1 WHAT IS CLAIMED IS:

- 2 1. A process for making an ethylene homopolymer having a polydispersity
3 above 4, and wherein the homopolymer is suitable for producing a film
4 having an MVTR below 0.4, which comprises contacting ethylene with a
5 catalyst comprising a cyclopentadienyl chromium hydrocarbyl compound
6 on a solid support, under slurry or gas phase polymerization conditions.
- 7 2. A process in accordance with Claim 1 wherein the film has an MVTR
8 below 0.3.
- 9 3. A process in accordance with Claim 1 wherein the film has an MVTR
10 below 0.25.
- 11 4. A process in accordance with Claim 1 wherein the polydispersity is
12 above 6.
- 13 5. A process in accordance with Claim 1 wherein the polydispersity is
14 above 7.
- 15 6. A process in accordance with Claim 1 wherein the CpCr compound is in
16 cationic form.
- 17 7. A process in accordance with Claim 1 wherein the chromium is in an
18 oxidation state of +3.
- 19 8. A process in accordance with Claim 1 wherein the catalyst includes a
20 co-catalyst comprising an aluminoxane.
- 21 9. A process in accordance with Claim 8 wherein the co-catalyst comprises
22 isobutyl aluminoxane.

1 10. A process in accordance with Claim 1 wherein the support comprises
2 silica and the weight percent chromium on the silica is between 0.5 and
3 1.5.

4 11. A process in accordance with Claim 1 wherein the polymerization is
5 carried out under slurry conditions.

6 12. A process in accordance with Claim 1 wherein the chromium compound
7 has the formula:



11 wherein $(C_5(R')_5)$ is a cyclopentadienyl or substituted cyclopentadienyl
12 ring;

13 R' is at each independent occurrence hydrogen, a hydrocarbyl radical
14 having 1-20 carbon atoms, or adjacent R' groups may together form one
15 or more rings;

16 X is a hydrocarbyl radical having 1-20 carbon atoms;

17 $a=1$ or 2 , $b=1$ or 2 where $a+b=3$;

18 $c=1$ or 2 with the proviso that when $c=2$ then X is alkyl;

19 L is at each independent occurrence a sigma donor stabilizing ligand;

20 $m=1$ to 2 inclusive; and

21 A is an anion.

- 1 13. A process in accordance with Claim 12 wherein the chromium
2 compound has the formula:



- 4 14. A process in accordance with Claim 13 wherein $(C_5(R')_5)$ is
5 pentamethylcyclopentadienyl.

Figure 1

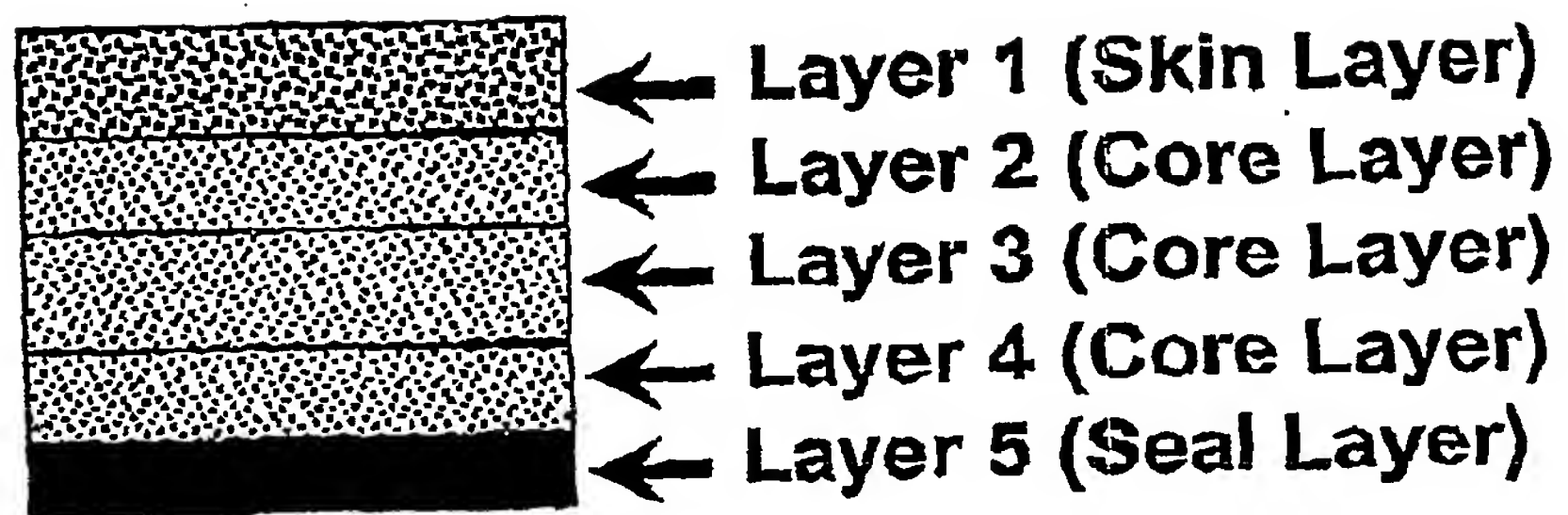
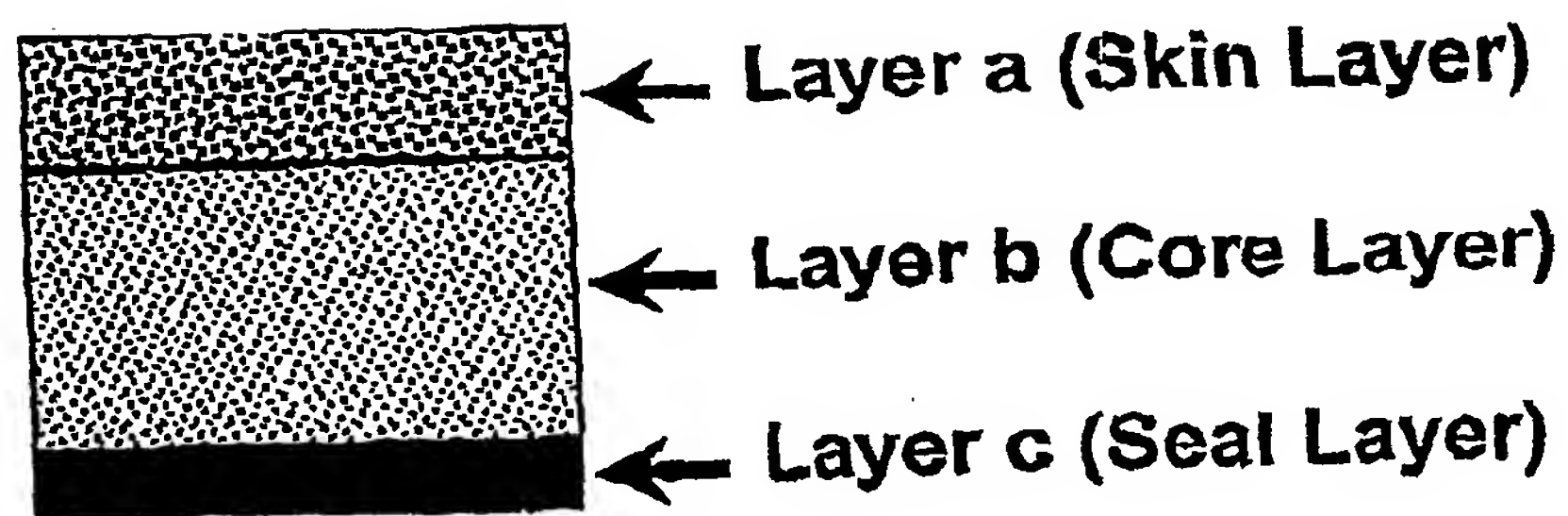


Figure 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/08436

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08F 4/02, 4/69, 4/78
US CL : 526/129, 160, 169, 352

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/129, 160, 169, 352

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EAST, WEST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,169,817 A (DAWKINS et al) 08 December 1992, Examples 1-10.	1-5, 11
X	US 5,418,200 A (CARNEY et al) 23 May 1995, Examples 1-25.	1-14

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

21 MAY 2001

Date of mailing of the international search report

07 JUN 2001

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